



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON CUPRIC OXYBROMIDE.

BY THEODORE WILLIAM RICHARDS.

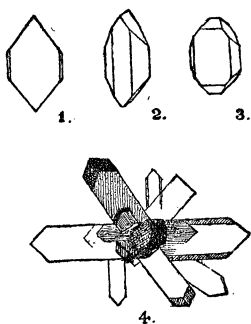
Presented by the Corresponding Secretary, October 8, 1890.

A CAREFUL examination of the basic bromide of copper precipitated by the solution of dried cupric bromide in water being an essential consideration in the preceeding research upon the atomic weight of copper, a quantity of the substance was gradually collected from successive preparations for the purpose of analysis.

The only mention of the preparation of a definite oxybromide of copper in chemical literature is that by Et. Brun,* who obtained a crystalline salt by the slow oxidation of a solution of cuprous bromide in aqueous potassic bromide, as well as by the action of the latter salt upon ammoniacal cupric sulphate. He describes his new preparation as consisting of very small dark green crystals totally insoluble in water, and gives several analyses of different samples which agree with the formula $\text{Cu}_2\text{Br}(\text{OH})_3$, or $3\text{CuO} \cdot \text{CuBr}_2 \cdot 3\text{H}_2\text{O}$. It seemed very probable that the substance under discussion was identical with this body, although prepared in a very different manner.

The oxybromide so often mentioned in the foregoing description of the research upon the atomic weight of copper crystallizes in very beautiful doubly terminated prisms, which undoubtedly belong to the trimetric system and have the varying habit shown in the accompanying sketch. When precipitated by the rapid addition of water to solid slightly basic copper bromide, the prisms appear as extremely thin plates (Fig. 1), often united in radiating groups; but on more gradual crystallization from stronger brown solutions, the crystals develop nearly equally in all axial directions (Figs. 2 and 3). The only angle even approximately measured with success by means of the microscope was that of the two domes upon each other, giving an

* *Compt. Rend.*, vol. cix. p. 66 (1889). Löwig and Berthémot describe an indefinite substance. *Liebig's Handw. Ch.*, iv. 714; *Ann. de Chim. et de Phys.*, [ii.] xlv. 385.



Magnified 250 diameters.

inclination of about $94\frac{1}{2}^\circ$ between the normals. This value affords us the means of calculating the axial ratio, $x : z = 1 : 1.08$; and the two figures suggest the angle $96^\circ 38'$ and axial ratio $1 : 1.123$ observed in atacamite.* Indeed, the general resemblance in habit and in emerald green color between the two substances is very marked, and has already been noticed by Brun.†

Crystallized cupric oxybromide which has been dried in the air does not lose weight over sulphuric acid. It is of course very soluble in mineral acids and in ammonia, as

well as in strong acetic acid. The mode of formation of the salt shows that it must be slightly soluble also in very concentrated solutions of the normal cupric bromide, and that dilution diminishes, or perhaps wholly destroys, this solubility. The proof of its total insolubility in water being of great importance in the preceding research, the following experiment was made.

Two hundred cubic centimeters of water were digested for four days at 25° with a tenth of a gram of very fine crystals of copper oxybromide, the mixture being occasionally shaken. The liquid was then filtered, and thirty cubic centimeters contained in a long tube were tested for copper with ammonia, giving an absolutely negative result. One hundred and thirty cubic centimeters of the same liquid were evaporated to dryness, and the apparently clean dish was rinsed with a few drops of dilute nitric acid, to which was then added an excess of ammonia. An exceedingly faint tinge only of blue was apparent, much less than that produced by one tenth of a milligram of copper under the same circumstances.

Being thus essentially insoluble in water, the oxybromide could hardly be present, even in traces, in the very dilute solution of cupric bromide used for the determination of the atomic weight; but for certainty upon this point the normal state of this solution was tested by experiments with methyl orange. These experiments, which have already been described,‡ settled the question in a wholly satisfactory manner.

* Zepharovitch, Wien. Akad. Sitzungsber., 1871, vol. lxiii. part i. p. 6.

† *Loc. cit.*

‡ This volume, page 201.

The salt is decomposed by continued boiling with water into the normal bromide and a dark insoluble compound of uncertain composition. Brun has already pointed out the fact that the crystals are quite decomposed when heated to 250°.

On account of the very small amount of substance at hand, the analysis was undertaken with all possible care.

- I. 0.20003 gram of copper oxybromide yielded, on evaporation with nitric and sulphuric acids and subsequent electrolysis, 0.09823 gram of metallic copper.
- II. 0.0828 gram of copper oxybromide yielded, on solution in ammonia, acidification with nitric acid, and precipitation by silver nitrate 0.0606 gram of argentic bromide.

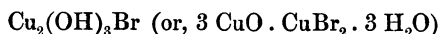
Analysis of Cupric Oxybromide.

	Theory. $\text{Cu}_2(\text{OH})_2\text{Br}$.	Found.		Average of Brun's results.
		I.	II.	
Copper	49.27	49.11		49.19
Bromine	30.98		31.15	31.05

The results agree with the theoretical as well as could be expected, considering the small quantities of substance used.

By the very slow oxidation of cuprous bromide, kept under water in the dark for six months, groups of emerald green radiating prisms over a tenth of a millimeter in length were obtained (Fig. 4), which by their terminal angles, color, and general appearance showed themselves to be identical with the compound whose analysis has just been given. The amount of these crystals was so small that it was impossible to determine their percentage composition, but there can be no doubt of its agreement with that given above. The crystalline salt was also obtained by the long continued action of cupric oxide upon a strong solution of cupric bromide.

It will be seen that the formula



does not exactly correspond to that of any one of the known oxychlorides, containing only three fourths as much water as atacamite ($3 \text{ CuO} \cdot \text{CuCl}_2 \cdot 4 \text{ H}_2\text{O}$). It is a noteworthy fact, however, that many of the more definite basic salts of copper contain, as these do, three molecules of copper oxide to every single molecule of the normal compound.